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Tailoring the corrosion resistance of Zn-Mn coating by electrodeposition from deep eutectic solvents

ABSTRACT

Well adhered, homogenous coatings were obtained from deep eutectic solvents (DES) based on choline chloride and urea, at current densities up to 20 mA cm^{-2}. The coatings' morphology was analyzed by atomic force microscopy, determining the agglomerates size and distribution. The corrosion stability of these deposits was analyzed in 3 wt. % NaCl solution by electrochemical impedance spectroscopy and polarization measurements, and compared with coatings deposited from a conventional water-based electrolyte. The influence of deposition current density and surface morphology, as well as of DES type, on the corrosion resistance was analyzed. It was shown that electrodeposition from DES enables incorporation of greater Mn amounts, that induced a pseudo-passivation effect, which, in turn, resulted in superior corrosion resistance.

Keywords: *electrochemical deposition, Zn-Mn alloy, coatings, deep eutectic solvent, corrosion stability.*

1. INTRODUCTION

The interest in the electrodeposition of Zn-Mn alloy coatings, mainly originates from the fact that these alloys may offer the best corrosion resistance among all Zn based coatings, so that they may be applied in anticorrosion protection of steel substrate [1, 2]. It is known that the corrosion behavior of electroplated Zn-Mn alloys is strongly affected by two independent factors, i.e. chemical (phase) composition and surface morphology [3]. Namely, the optimal corrosion resistance is achieved when the Mn content in the alloy reaches a certain minimum level, on the one side, and on the other side, when the electrodeposited coating is pore and defect free [4].

The Zn-Mn coatings have been traditionally electrodeposited from aqueous electrolytes of various types [1,2,3,4]; however these baths suffer

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from the parasitic hydrogen evolution reaction, low current efficiency, and poor morphology of high-Mn alloy deposits. Recently it has been proven that the successful Zn-Mn deposits may be obtained from deep eutectic solvents (DES) based on choline chloride and urea, at Pt, Cu, or steel substrates [5, 6, 7]. Deep eutectic solvents are electrolytes consisting entirely of ions; they possess lower conductivity and higher viscosity, but usually wider electrochemical window as compared to aqueous solutions, so they are suitable electrolytes for electroreduction of electronegative elements like Mn [8].

In our previous work it was shown that the alloys with as high as 25 wt.% Mn, and compact surface morphology, may be deposited from choline chloride-urea DES, and such coatings could be excellent candidates for an increased corrosion resistance in aggressive media [6]. Therefore, this work presents the analysis of the corrosion resistance of various Zn-Mn samples obtained from choline chloride-urea DES, on steel. There is only one report on the corrosion behavior of the Zn-Mn obtained from DES and the coatings were deposited on copper substrate [5], so we believe that this is the first work on analysis of Zn-Mn coatings on steel obtained from DES.

2. EXPERIMENTAL

Choline chloride (Aldrich, 99%), urea, zinc chloride (Aldrich, >98%), and manganese (II) chloride ($MnCl_2 \cdot 4H_2O$) (Aldrich, >99%) were used as obtained. The eutectic mixture was formed at 70 °C until a homogeneous colorless liquid was observed, by stirring the dried choline chloride with the urea hydrogen bond donor mixture in a 1:2 molar ratio. The plating electrolytes were formed by adding appropriate quantities of manganese (II) chloride and zinc chloride to the deep eutectic solvent and stirring the mixture at 70 °C until homogeneous electrolytes referred to as DES 1:1 (0.1 mol dm^{-3} $MnCl_2$, 0.1 mol dm^{-3} $ZnCl_2$) and DES 3:1 (0.3 mol dm^{-3} $MnCl_2$, 0.1 mol dm^{-3} $ZnCl_2$) were obtained.

The electrodeposition of Zn-Mn coatings was carried out at 60 °C using a steel working electrode (8 cm^2) and a high purity zinc counter electrode. The coatings were deposited galvanostatically, using potentiostat PAR M273A, at 3, 8, 12 or 20 mA cm^{-2} from each of the two electrolytes (DES 1:1 and DES 3:1). The electrodeposition time was adjusted to obtain deposits of the same thickness by maintaining the same electrodeposition charge density in each experiment. The steel electrode was mechanically prepared using abrasive emery papers down to 2000 grit, degreased in a saturated solution of NaOH in ethanol, pickled with 2 mol dm^{-3} HCl for 30 s, and finally rinsed with distilled water, acetone and dried in air by a fan. After electrodeposition, the samples were cleaned with acetone and dried in air by a fan.

In order to study the coating morphology by atomic force microscopy (AFM), NanoScope 3D (Veeco, USA) microscope was used, which operated in tapping mode under ambient conditions. Etched silicon probes with spring constant 20 – 80 Nm^{-1} were used. AFM images were recorded over different scan areas. The agglomerate size dimension of electrodeposited coatings was determined from AFM image profile line analysis. In order to calculate the agglomerate size distribution, hundred agglomerates were measured on each AFM image. In addition, the surface morphology and composition of the samples were analyzed by a JEOL JSM 5800 scanning electron microscope (SEM), operated at 20 keV, equipped with an Oxford Instruments energy dispersive X-ray spectrometer (EDS).

Corrosion measurements were performed in an aerated 3 wt.% NaCl solution. A classic three-electrode cell with a platinum plate as counter electrode, a Zn-Mn coating (1 cm^2) as a working electrode and a saturated calomel electrode as reference, was used. The corrosion rates of the deposited Zn-Mn alloys were determined using extrapolation of anodic polarization curves to the open circuit potential (OCP). Potential sweep rate of 0.2 mV s^{-1} was applied starting from −250 mV vs. OCP and ending at +250 mV vs. OCP, after the constant OCP was established (60 min). In addition, electrochemical impedance spectroscopy (EIS) measurements were obtained at the OCP in a frequency range of 100 kHz − 0.01 Hz, with an applied AC signal amplitude perturbation of 10 mV, and the corresponding Nyquist plots were analyzed.

3. RESULTS AND DISCUSSION

3.1. Surface morphology

It was shown previously [9, 10] that the highest corrosion resistance of Zn-Mn alloy is achieved when the Mn content is in the range 20 − 40 wt.%, and when the film is compact and smooth. Therefore, the first part of the analysis was related to finding the relation between the deposition current density and the surface morphology of the Zn-Mn coatings. The Mn content in the electrodeposited samples, as determined by EDS method, is shown in Table 1.

Table 1. The dependence of chemical composition and corrosion parameters of Zn-Mn coatings, on the electrodeposition parameters

Tabela 1. Zavisnost hemijskog sastava i parametara korozione stabilnosti Zn-Mn prevlaka, od parametara taloženja

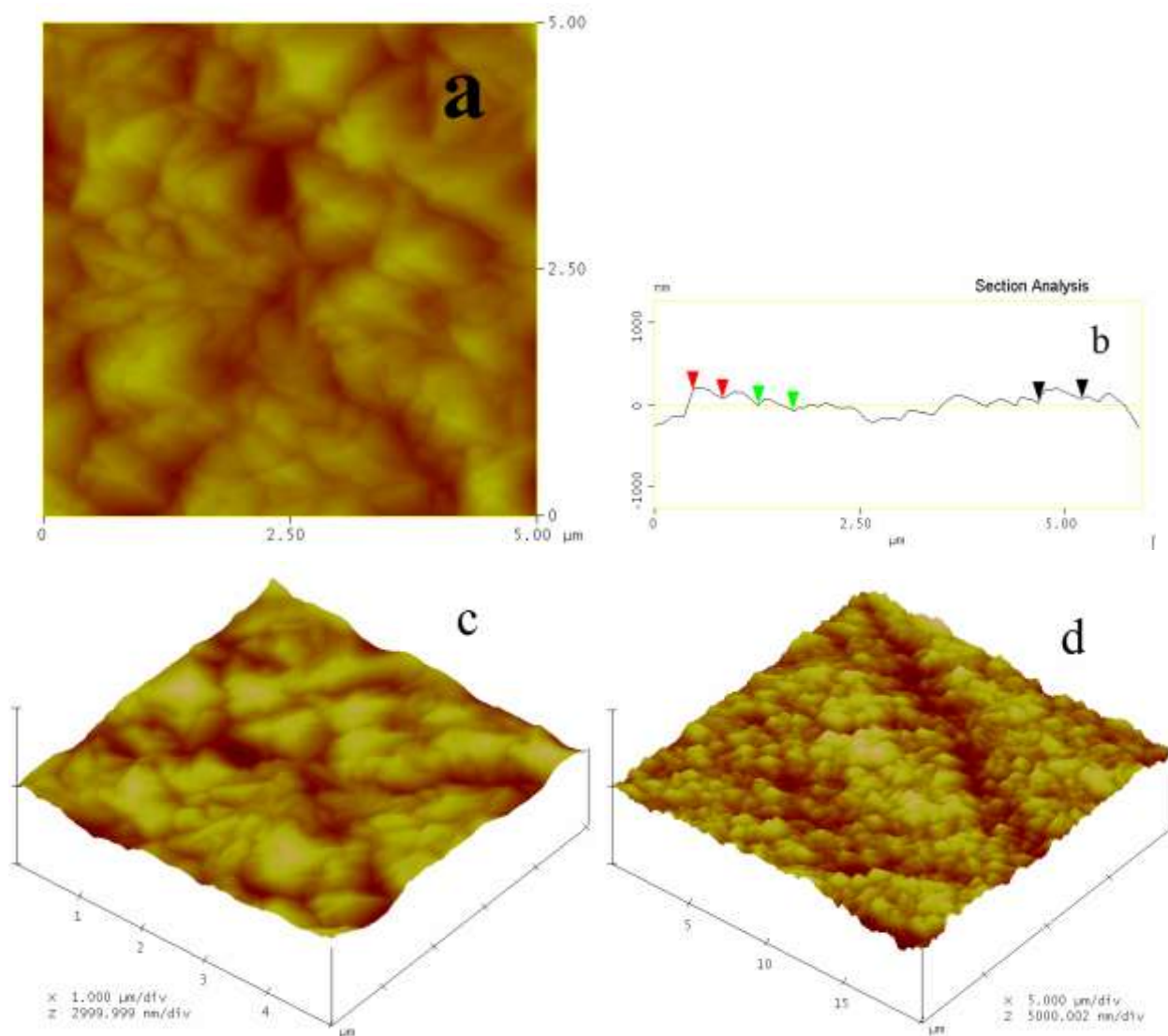| DES	j_{dep} / mA cm^{-2}	$-E_{corr}$ (V$_{SCE}$)	j_{corr}/ μA cm^{-2}	Mn wt.%
1:1	3	1.110	1.06	25
	5	1.060	1.5	28
	8	1.040	3.2	25
	12	1.045	3.6	24
	20	1.030	5.1	20
3:1	3	1.130	0.90	33
	8	1.040	0.82	33
	12	1.046	5.3	29

Figure 1. a) 2D; b) cross section height profile analysis; and 3D AFM images of the scanned area of: c) 25 μm² and d) 400 μm² of the Zn-Mn films deposited from DES 1:1 at 3 mA cm⁻²

Slika 1. a) 2D; b) linije profila visine; i 3D AFM mikrofotografije skenirane površine: c) 25 μm² i d) 400 μm² Zn-Mn prevlaka dobijenih taloženjem iz DES 1:1 gustinom struje 3 mA cm⁻²

Well adhered, homogenous coatings were obtained from deep eutectic solvent based on choline chloride and urea, at current densities up to 20 mA cm⁻², as presented in Figs. 1 – 4. The surfaces obtained at low deposition current densities (2, 3 and 8 mA cm⁻²) are compact and smooth, as can be seen from Figs. 1 and 2 for coatings deposited at 3 and 8 mA cm⁻², respectively.

The crystallites formed at 3 mA cm⁻² (Fig. 1) group in agglomerates ranging 800 – 1000 nm that are uniformly distributed over the deposit. Quite similar morphology is shown for alloy coating deposited at 8 mA cm⁻² (Fig. 2), with agglomerates averaging about 700 nm.

The increase in c.d. results in the coarsening of the deposit and increasing the size of agglomerates, as shown in Figs. 3 and 4 for deposits obtained at 12 and 20 mA cm⁻². As section analysis clearly presents, the agglomerates of up to 2.5 μm are formed at higher deposition current densities.

The figures 1 – 4 evidence the trend very similar to the one observed in aqueous solutions [2, 3]. Namely, bigger agglomerates are formed at higher deposition current density.
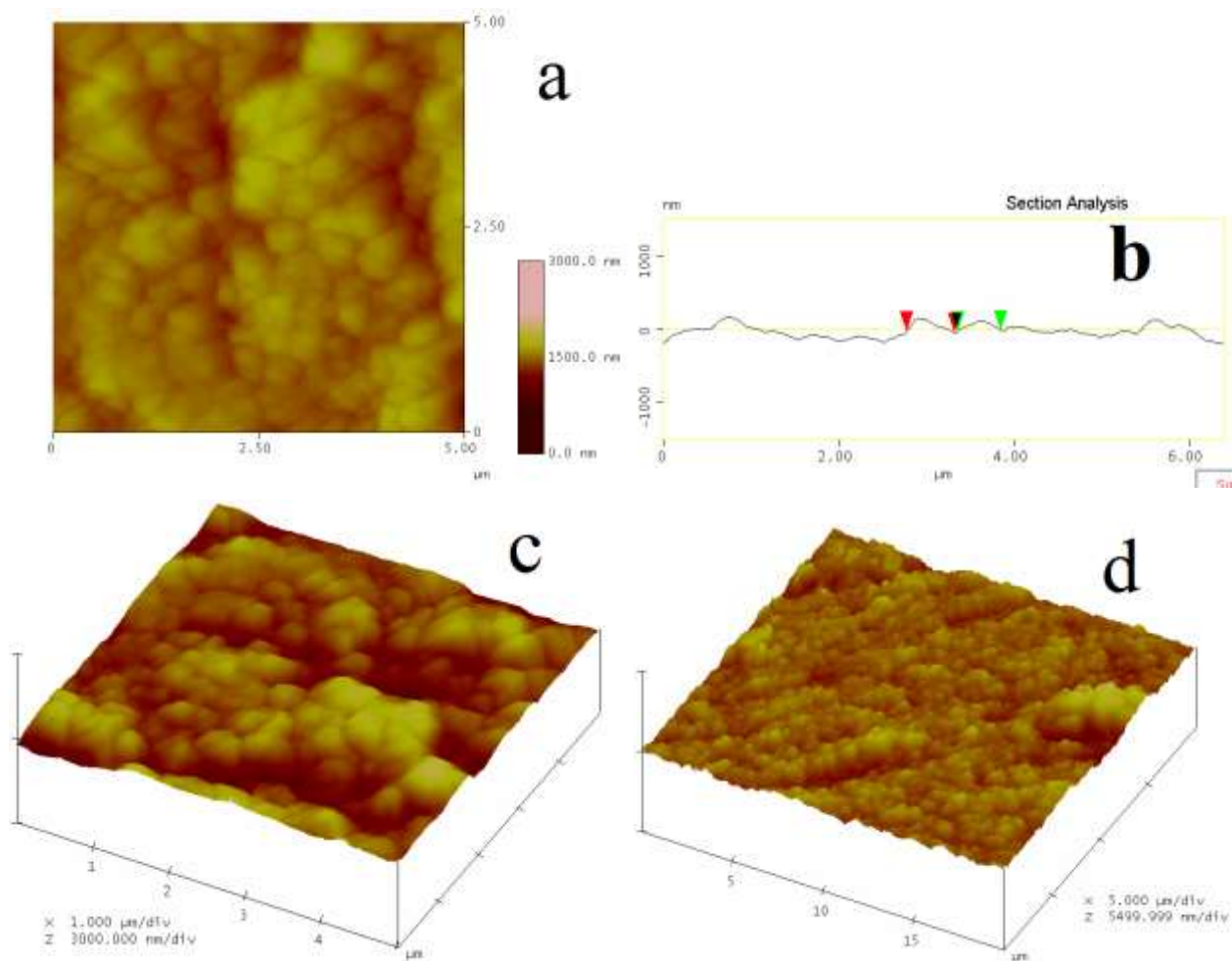
Figure 2. a) 2D; b) cross section height profile analysis; and 3D AFM images of the scanned area of: c) 25 μm² and d) 400 μm² of the Zn-Mn films deposited from DES 1:1 at 8 mA cm⁻²

Slika 2. a) 2D; b) linije profila visine; i 3D AFM mikrofotografije skenirane površine: c) 25 μm² i d) 400 μm² Zn-Mn prevlaka dobijenih taloženjem iz DES 1:1 gustinom struje 8 mA cm⁻²
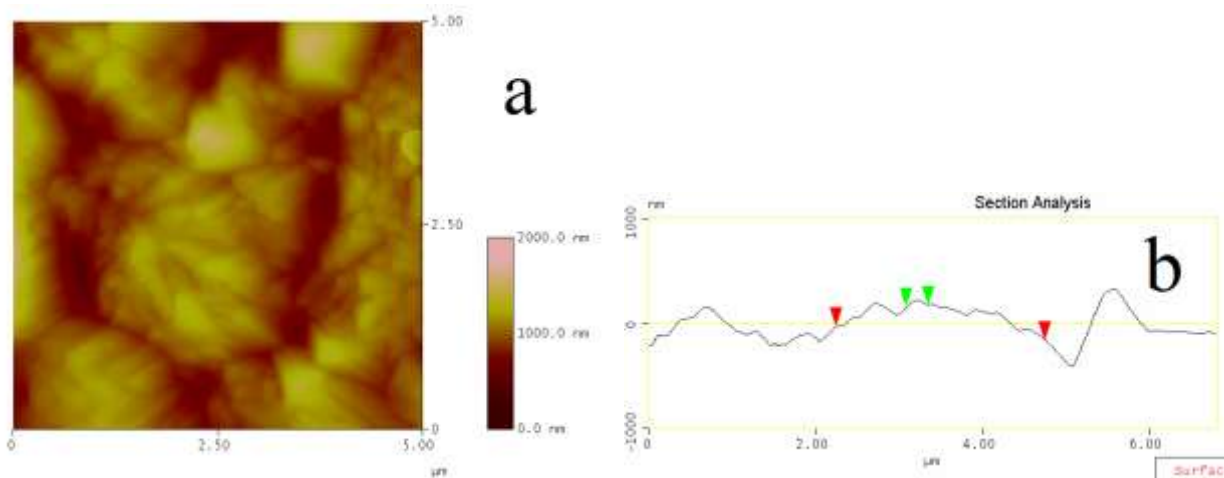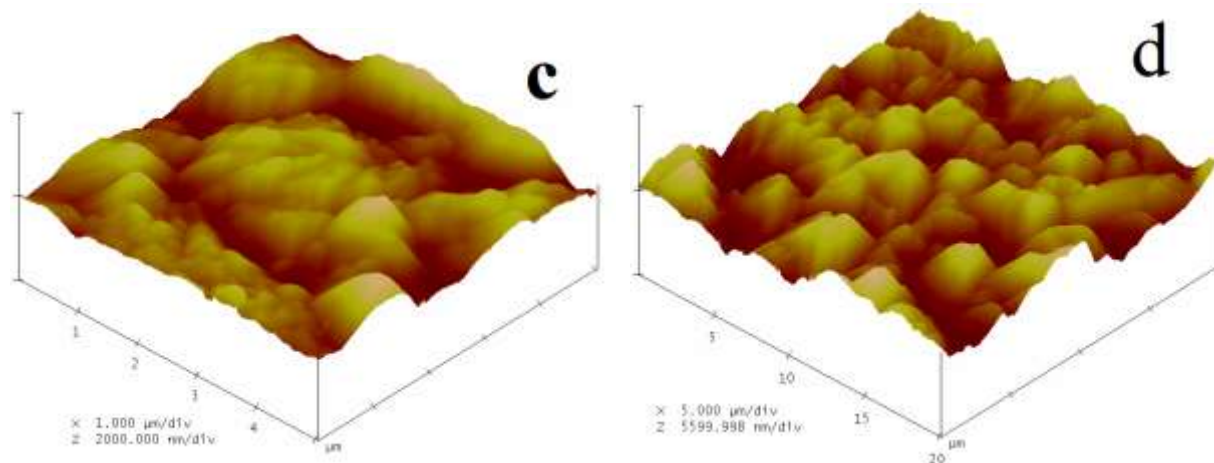

Figure 3a   *Figure 3b*

Figure 3. a) 2D; b) cross section height profile analysis; and 3D AFM images of the scanned area of: c) 25 µm² and d) 400 µm² of the Zn-Mn films deposited from DES 1:1 at 12 mA cm⁻²

Slika 3. a) 2D; b) linije profila visine; i 3D AFM mikrofotografije skenirane površine: c) 25 µm² i d) 400 µm² Zn-Mn prevlaka dobijenih taloženjem iz DES 1:1 gustinom struje 12 mA cm⁻²
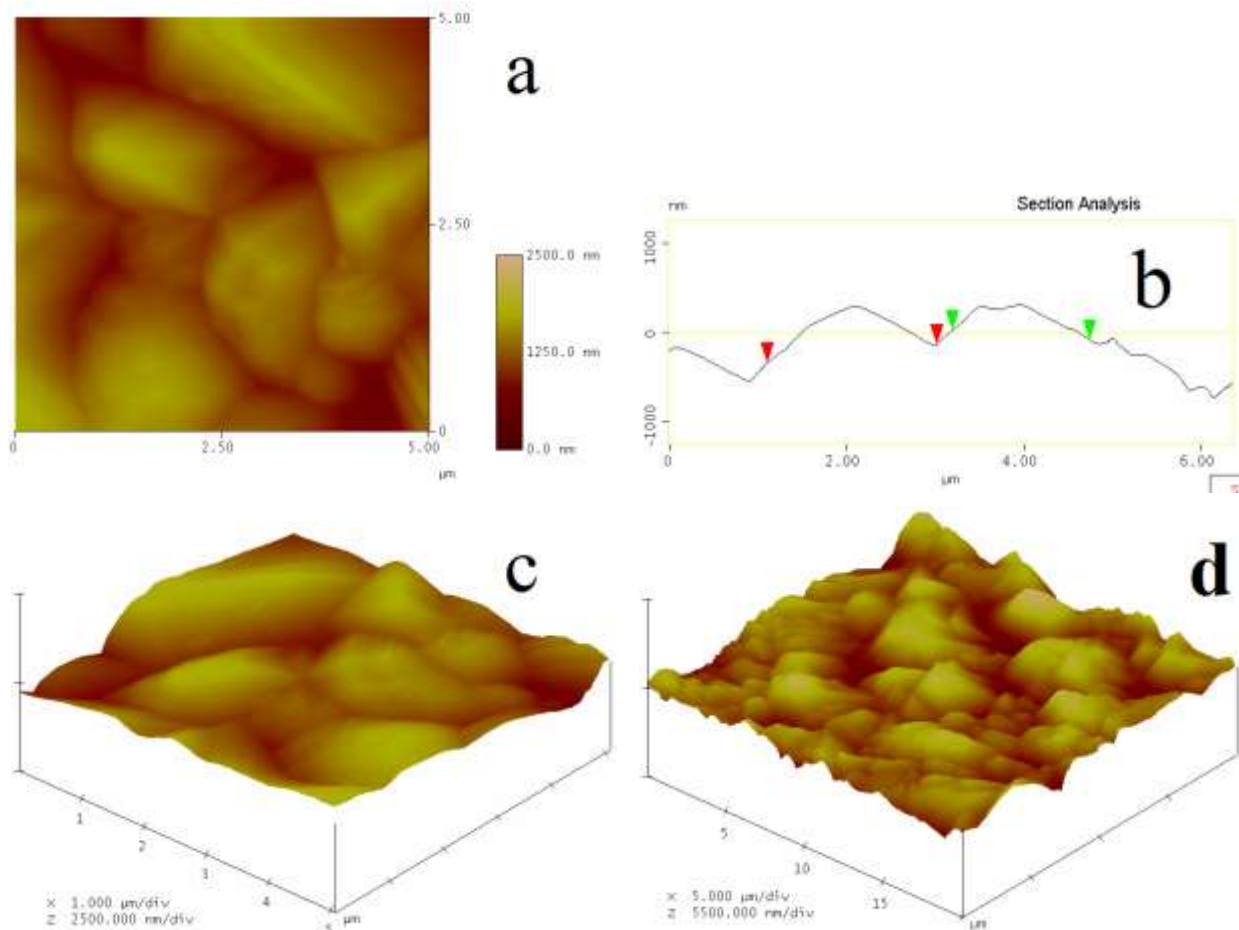

Figure 4. a) 2D; b) cross section height profile analysis; and 3D AFM images of the scanned area of: c) 25 µm² and d) 400 µm² of the Zn-Mn films deposited from DES 1:1 at 20 mA cm⁻²

Slika 4. a) 2D; b) linije profila visine; i 3D AFM mikrofotografije skenirane površine: c) 25 µm² i d) 400 µm² Zn-Mn prevlaka dobijenih taloženjem iz DES 1:1, gustinom struje 20 mA cm⁻²

The influence of the DES type is shown in Fig. 5 for alloy coating deposited from 3:1 DES at 20 mA cm⁻². Considerably smaller agglomerates of about 60 nm could be noticed at Fig. 5.
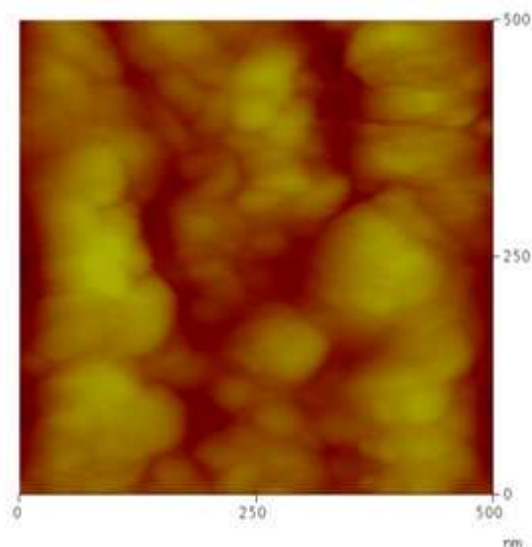

Figure 5. 2D AFM image of the scanned area of 0.25 µm² of the Zn-Mn film deposited from DES 3:1 at 20 mA cm⁻²

Slika 5. 2D AFM mikrofotografija skenirane površine 0.25 µm² Zn-Mn prevlake dobijene taloženjem iz DES 3:1 gustinom struje 20 mA cm⁻²

From the AFM images the agglomerate size distribution was determined and it is shown in Fig. 6. The majority of the agglomerations in the coating deposited at 3 mA cm⁻² (Fig. 6a) are of about 800 nm. The morphology of the coating deposited at high current density of 20 mA cm⁻² (Fig. 6b) is made up of considerably larger agglomerates, averaging 1.5 µm. Deposition from the solution with higher Mn content (DES 3:1) at 3 mA cm⁻² resulted in fine agglomerates, dominated by the ones of up to 80 nm (Fig. 6c).

The comparison of the surface morphologies obtained at high c.d. (20 mA cm⁻²) from the two different electrolytes, shows a remarkable difference in the agglomeration size. The DES with lower Mn²⁺ ion content, produces the surface with larger agglomerates, and vice versa. It may be assumed that this is the consequence of the influence of Mn²⁺ ion concentration, on the nucleation process during the coating growth. Namely, it was shown in [6] that the higher Mn²⁺ ion concentration in reline, results in higher overpotential for all cathodic processes. Furthermore, it is known [11] that higher overpotential during metal electroreduction, enables easier formation of new crystal nuclei, rather than their agglomeration, which eventually leads to a smoother surface with small crystalline

grains. We assume that this is the case in DES 3:1, i.e. the high cathodic overpotential due to the high concentration of Mn²⁺ ions, results in small agglomerates and higher Mn content.
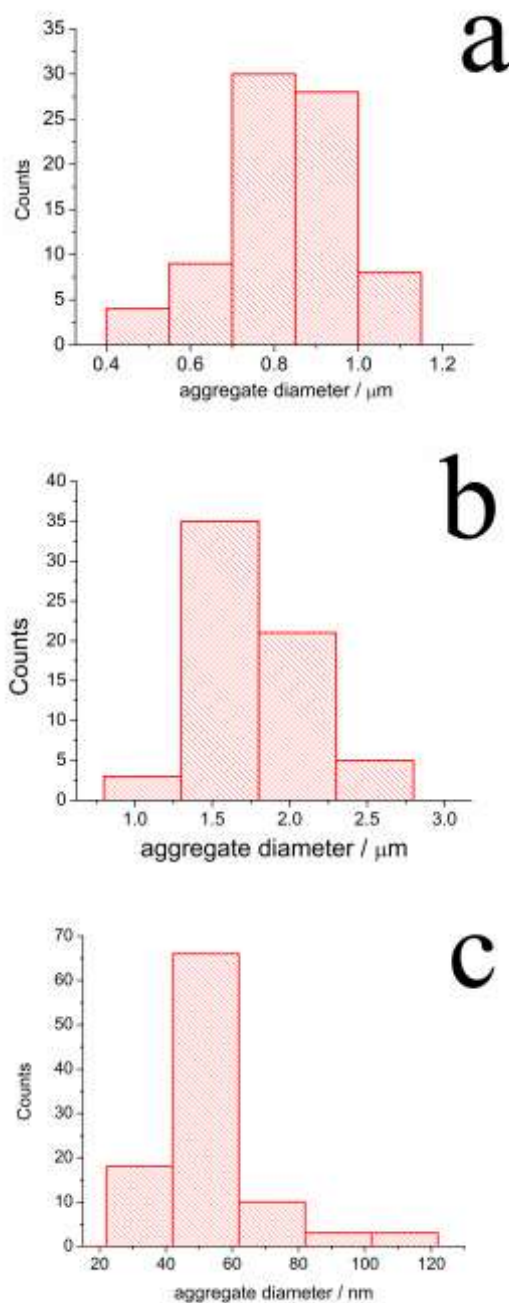

Figure 6. Aggregate size (AFM data) distribution of the Zn-Mn coatings electrodeposited from DES 1:1 at a) 3 and b) 20 mA cm⁻², and from DES 3:1 at c) 3 mA cm⁻².

Slika 6. Raspodela veličine aglomerata (iz AFM podataka) na Zn-Mn prevlakama dobijenim taloženjem iz DES 1:1 gustinom struje a) 3 i b) 20 mA cm⁻², i iz DES 3:1 gustinom struje c) 3 mA cm⁻².

Besides the similarities between the electrodeposition process in aqueous and in DES, the main benefit of using DES is the fact that at much lower deposition current density (in the range when the compact deposit is formed), the high Mn content in the alloy is achieved. Namely, due to the intensive hydrogen evolution in aqueous electrolytes, electrodeposited Zn-Mn coatings could hardly incorporate larger amounts of Mn. Deposition from DES enables formation of Mn rich alloys at considerably lower c.d.

3.2 Corrosion resistance

To evaluate the corrosion resistance of the Zn-Mn alloys, coatings were deposited at different current densities, from the two electrolyte types (DES 1:1 and DES 3:1), on steel substrate. The corrosion resistance was evaluated by polarization measurements in 3 wt.% NaCl solution. Figure 7 presents the potentiodynamic polarization curves obtained for several representative samples, while Table 1 shows the results obtained from the Tafel evaluation of the corrosion parameters of the coatings.
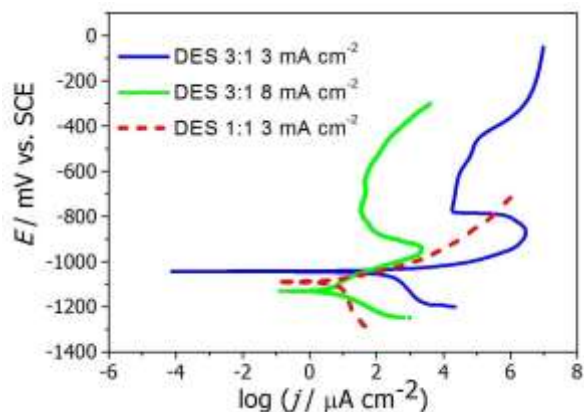

Figure 7. Tafel polarization curves in 3% NaCl solution for Zn-Mn alloy coatings obtained at different current densities, from DES 1:1 and DES 3:1

Slika 7. Polarizacione krive u 3% NaCl za Zn-Mn prevlake dobijene taloženjem različitim gustinama struje, iz DES 1:1 i DES 3:1

Tafel polarization curves for Zn–Mn alloy deposits show some differences, not only depending on the deposition c.d. but also on the type of DES. Polarization curves for alloy coatings deposited from DES with 1:1 ratio, at low current density, show behavior typical of Zn coatings in NaCl solution. The anodic curve corresponds to the dissolution of alloy coating (active zone). The values of corrosion c.d. (j_{corr}) are not so much influenced by the type of DES, but more by deposition current density. In the case of Zn–Mn with greater amount of Mn, deposited from the 3:1 DES, values are of the similar magnitude like alloy

coatings with small Mn content, as well as bare Zn deposits. However, a pseudo passivation effect induced by the high Mn content could also be observed, reducing the oxidation rate.

Besides the fact that Zn-Mn is thermodynamically less noble than Zn, it is reported that Zn-Mn shows a passivating behavior in various corrosive environments due to the formation of insoluble Mn-compounds on the corroding surface which affects the catalytic activity for cathodic oxygen reduction. Generally, passivation is associated with the formation of a barrier layer. This barrier layer slows down the diffusion of corrosive species and thus, reduces the corrosion reaction. In addition, the barrier layer forms when the dissolution of a metal produces the condition in which the solubility of the salt, hydroxide or oxide, in the electrolyte near the electrode surface is exceeded and a solid film forms. It can be concluded from the Tafel plots that the highest corrosion resistance, followed by pseudo passive behavior, is achieved for the high Mn content (33 wt. %, Fig. 7) and the compact surface morphology consisting of small aggregates (Fig. 5) for alloy coatings deposited from 3:1 DES.

The EIS studies were carried out on representative Zn-Mn coatings after 5 h of continuous immersion into the 3 wt.% NaCl solution, and Fig. 8 shows the EIS spectra (Nyquist plots) of the several samples, recorded at the open circuit potential. All diagrams show a semi-circle arc in the high-frequency range, followed by the second, not completed, semi-circle arc. The diameter of the two semicircles is associated with the corrosion product (passive) film resistance, and the charge transfer resistance of the corrosion reaction under the passive film, which may be correlated to the corrosion rate [12].

The electrical resistance of the corrosion product films and the corrosion resistance of the Zn-Mn coatings is related to the respective high- and low-frequency impedance diameters, where a semicircle with larger diameter indicates higher corrosion resistance. As seen in Fig. 8, the semicircle diameters depend both on deposition c.d. and the DES type. In the ionic liquid with lower Mn^{2+} concentration (DES 1:1, Fig. 8a), the highest corrosion resistance is observed for the lowest deposition c.d. investigated (3 mA cm^{-2}). On the contrary, in DES 3:1 (Fig. 8b), the best corrosion performance is achieved for the Zn-Mn alloy deposited at 8 mA cm^{-2}. When the AFM images (Figs. 1 - 5) and the chemical composition of the alloys (Table 1) are compared, it may be concluded that the high Mn content is beneficial for the high corrosion resistance, as well as smooth and compact morphology. To support this conclusion, the impedance spectroscopy was compared for the

Zn-Mn coating obtained from typical, chloride salt containing aqueous electrolyte [4, 9], to the one with high Mn content, deposited from DES 3:1 (Fig. 8c). It is clear that the sample with high Mn, obtained from DES, provides much better corrosion performance.
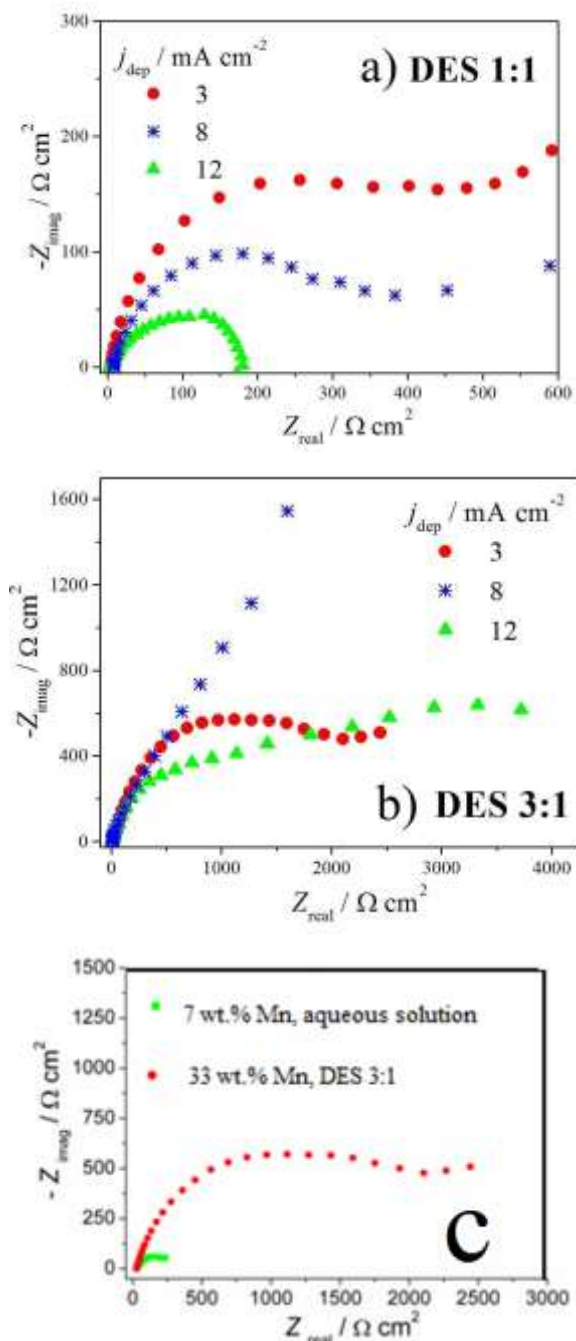

Figure 8. Nyquist plots of Zn-Mn coatings electrodeposited from: a) DES 1:1, b) DES 3:1, and c) aqueous and DES 3:1 electrolytes.

Slika 8. Najkvistovi dijagrami za Zn-Mn prevlake elektrohemijski taložene iz: a) DES 1:1, b) DES 3:1, i c) vodenog rastvora i DES 3:1

4. CONCLUSIONS

This study examined the relation between the corrosion resistance, the morphology and chemical composition of Zn-Mn alloy coatings obtained from deep eutectic solvent-based electrolytes, under different electrodeposition current densities and different Mn^{2+} to Zn^{2+} ions ratio. The Tafel polarization plots and the SEI measurements showed that the Zn-Mn alloys with high Mn content have a passivating behavior, and their corrosion performance depends strongly on their chemical composition and morphology. The Zn-Mn alloys deposited from DES 3:1 electrolyte at 8 mA cm^{-2} showed the best corrosion resistance and this was attributed to a sufficiently high Mn content on one side, and a smooth and compact morphology on the other side. The EDS analysis shows that starting from the deposition c.d. of 3 mA cm^{-2}, the Mn content in the alloy reaches 25 wt.%, and does not change significantly with the increase in deposition c.d.

5. REFERENCES

[1] Z. Ortiz, P. Díaz-Arista, Y. Meas, R. Ortega-Borges, G. Trejo (2009) Characterization of the corrosion products of electrodeposited Zn, Zn–Co and Zn–Mn alloys coatings, Corr. Sci., 51, 2703–2715.

[2] M. Bučko, J. Rogan, S.I. Stevanović, S. Stanković, J.B. Bajat (2013) The influence of anion type in electrolyte on the properties of electrodeposited Zn-Mn alloy coatings, Surf. Coat. Technol., 228, 221–228.

[3] M. Bučko, J. Rogan, S.I. Stevanović, A. Perić-Grujić, J.B. Bajat (2011) Initial corrosion protection of Zn–Mn alloys electrodeposited from alkaline solution, Corr. Sci., 53, 2861–2871.

[4] S. Ganesan, G. Prabhu, B.N. Popov (2014) Electrodeposition and characterization of Zn-Mn coatings for corrosion protection, Surf. Coat. Technol., 238, 143–151.

[5] S. Fashu, C.D. Gu, J.L. Zhang, H. Zheng, X.L. Wang, J.P. Tu (2015) Journal of Materials Engineering and Performance, 24, 434–444.

[6] M. Bučko, D. Culliton, A.J. Betts, J.B. Bajat (2017) The electrochemical deposition of Zn–Mn coating from choline chloride–urea deep eutectic solvent, Trans. IMF, 95(1), 60-64.

[7] P. Chung, P. Cantwell, G. Wilcox, G. Critchlow (2008) Electrodeposition of zinc–manganese alloy coatings from ionic liquid electrolytes, Trans. IMF, 86, 211–219.

[8] A. Abbott, G. Capper, D. Davies, K. McKenzie, S. Obi (2006) Solubility of metal oxides in deep eutectic solvents based on choline chloride, J. Chem. Eng. Data, 51, 1280–1282.

[9] C. Muller, M. Sarret, T. Andreu (2002) Electrodeposition of Zn-Mn alloys at low current densities, J. Electrochem. Soc., 149, C600–C606.

[10] C. Muller, M. Sarret, T. Andreu (2003) ZnMn alloys obtained using pulse, reverse and superimposed

current modulations, Electrochim. Acta, 48, 2397–2404.

[11] R. Ramanauskas (1999) Structural factor in Zn alloy electrodeposit corrosion, Appl. Surf. Sci., 153, 53-64.

[12] S. Manov, A.M. Lamazouere, L. Aries (2000) Electrochemical study of the corrosion behavior of zinc treated with a new organic chelating inhibitor, Corr. Sci., 42,1235–1248.

IZVOD

POBOLJŠANJE KOROZIONE POSTOJANOSTI Zn-Mn PREVLAKE, ELEKTROHEMIJSKIM TALOŽENJEM IZ DUBOKIH EUTEKTIČKIH SMEŠA

Elektrohemijskim taloženjem iz eutektičke smeše na bazi holin hlorida i uree, gustinama struje taloženja do 20 mA cm^{-2} dobijene su homogene prevlake Zn-Mn legure, dobre adhezije na čeliku. Morfologija dobijenih prevlaka je ispitivana mikroskopijom međuatomskih sila. Određene su veličine aglomerata kristalnih zrna i njihova raspodela po površini u zavisnosti od vrste rastvora za taloženje i gustine struje taloženja. Koroziona stabilnost prevlaka legura je ispitivana spektroskopijom elektrohemijske impedancije i polarizacionim merenjima u rastvoru 3 % NaCl i upoređena je sa svojstvima prevlaka dobijenih elektrohemijskim taloženjem iz vodenih rastvora. Pokazan je uticaj gustine struje taloženja, morfologije prevlaka, kao i vrste eutektičke smeše, na otpornost elektrohemijski taloženih prevlaka legura prema koroziji. Elektrohemijskim taloženjem iz eutektičkih smeša je moguće dobiti prevlake Zn-Mn legure sa većim sadržajem Mn, koje dovode do pojave pseudo-pasivnog sloja na površini, povećavajući njihovu korozionu stabilnost.
Ključne reči: *elektrohemijsko taloženje, Zn-Mn legure, eutektičke smeše, koroziona stabilnost*